Development of Materials for High Energy Batteries

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Outline

- **Metal Phosphate Coating for Improved Cathode Material Safety**

  Funded by NASA Johnson Space Center and NASA Glenn Research Center under contract # NNC09CA04C. COTR: Dr. Judith Jeevarajan.

  – Motivation and Coating Benefits

  – Program Results

- Electrochemical Performance of Silicon Whisker and Carbon Nanofiber Composite Anode

  Funded by NASA Glenn Research Center under contracts NNX09CD30P and NNX10CA51C. COTR: Dr. Richard Baldwin.

- Summary and Next Steps

Focus\Accomplishments for Year 2 of the Program

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Application and scale-up of the coating developed in year 1 to NASA's specified mixed metal oxide cathode material (TODA MNC-9100) in order to support evaluation in cells constructed by NASA's commercialization partner. Demonstration of the cycling and safety performance characteristics of the PSI coated cathode material.

- Optimized coating procedures for coating TODA cathode material.
- Coating reduces exotherms observed on heating delithiated cathode material.
- Coated cathodes demonstrated <1% loss in discharge capacity over 50 cycles at a C/5 rate.
- Demonstrated scale-up with construction of 1Ah pouch cells:
  - **No reduction in discharge capacity or voltage observed.**
  - **On abuse testing pouch cells utilizing coated cathode material demonstrated improved stability.**
- Successfully scaled-up cathode coating to produce and deliver 1500grams of coated cathode material.

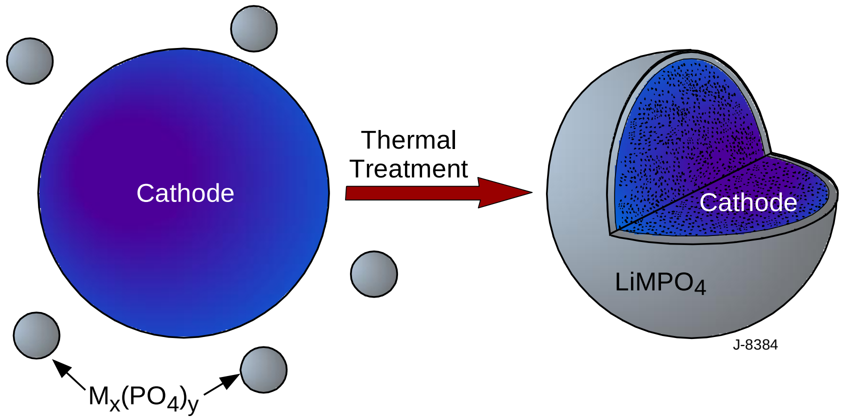
Motivation

Problem:

- Under abuse conditions, exothermic reactions between high voltage cathode materials and the battery electrolyte can lead to catastrophic failure.

Remediation Approach:

- PSI formed lithium metal phosphate coatings on metal oxide cathodes by thermal treatment of a mixture of metal phosphate and the cathode.[1]



[1]PSI patenting pending process.

Benefits of the Lithium Metal Phosphate Coating

- Coating is a lithium conductor.
- Metal phosphates offer greater stability than their metal oxide counterparts.
- Coating technique can be applied to protect any high energy density cathode material.
- Common processing steps allowing for low cost manufacturing.

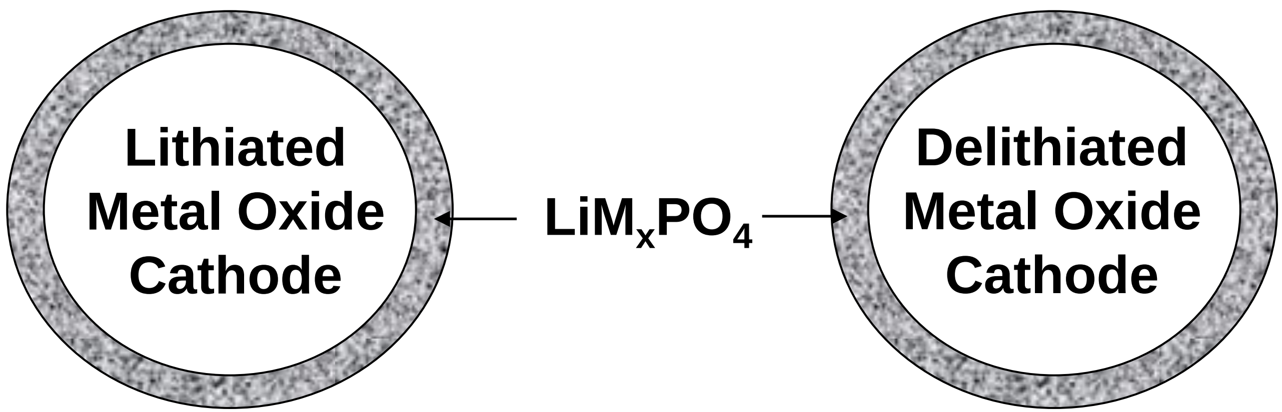
Key Benefit: Cathode Surface Oxidation State

- For high voltage cathode materials:

  V_{Mox} (Oxidized Metal Potential) > $V_{El\text{-}limit}$ (Stability limit of the Electrolyte)

- Results in spontaneous oxidation of the electrolyte.

- For coated material, the lithium metal phosphate layer remains in the reduced form upon full charge.



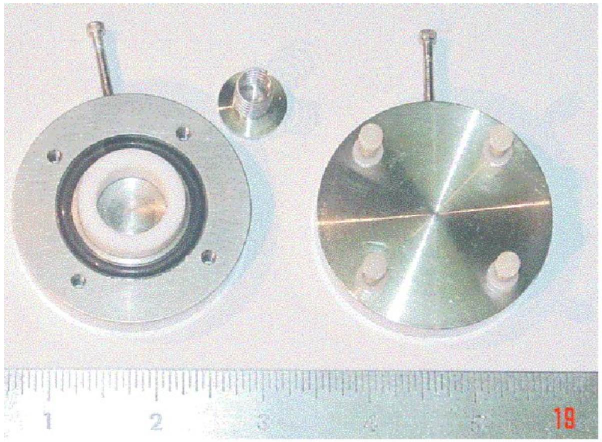
Discharge **Charged**

DSC Testing Technique

DSC (differential scanning calorimetry) tests were performed to demonstrate the effect of the coating on the thermal stability of the cathode material in its delithiated state.

Testing Technique:

- Half-cells (with a lithium counter) were built using PSI's puck cell fixture and charged to 4.8V at 12.5mA/g (a C/20 rate).
- Cathodes were harvested and rinsed with DMC. DSC tests were performed after drying.
- Small punches were taken from the cathode and sealed in the DSC pans.
- All DSC pans were pre-run from 25-350°C at 5°C/min to provide a baseline.



G-7333

Spring Loaded Puck Cell

J-8411

DSC Sample Pans

Heat Flow vs. Temperature for Dry, Delithiated Uncoated and Phosphate Coated TODA Cathode Material

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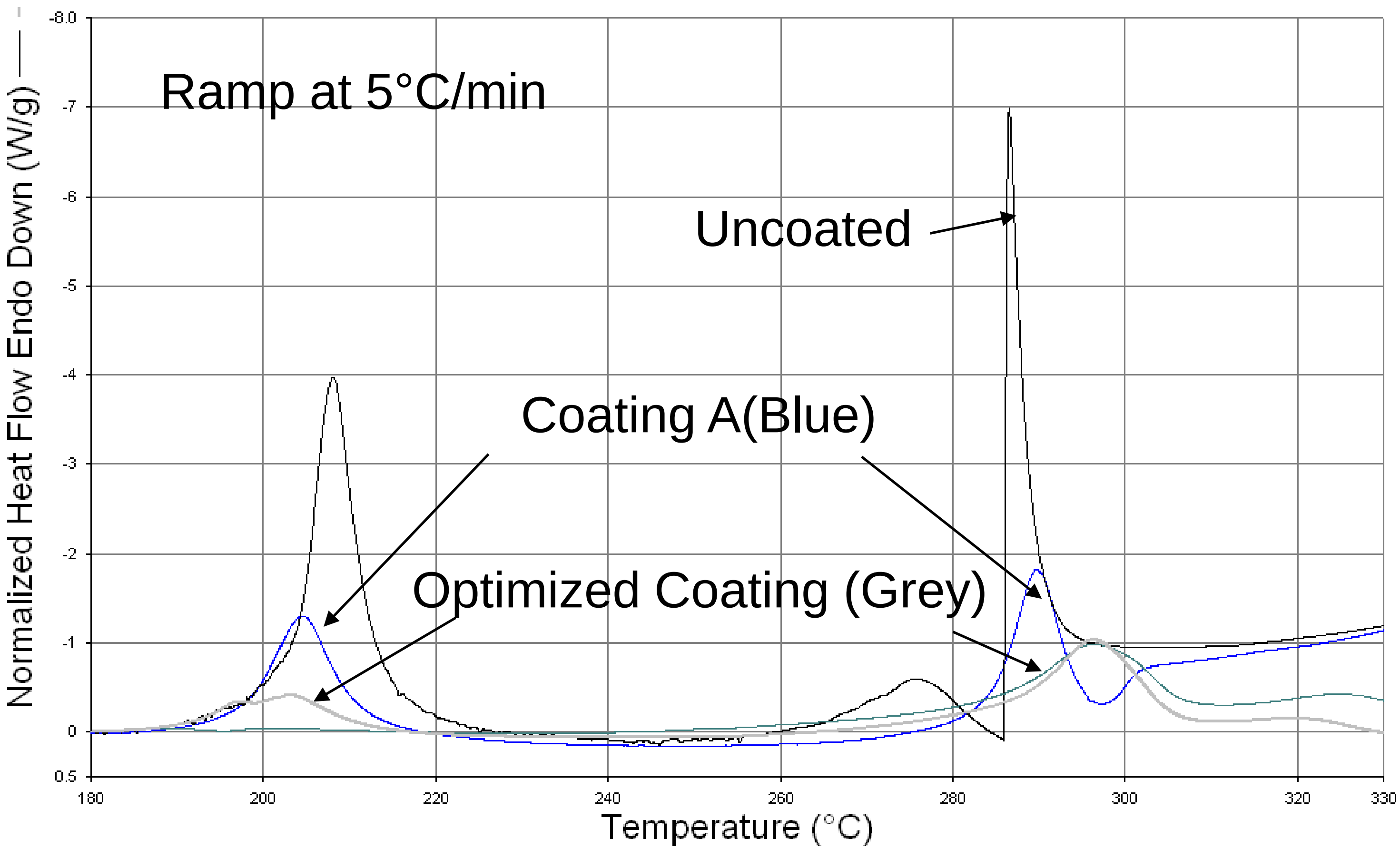
- Coatings adjusted to minimize phosphate content.
- All exotherms are muted with exotherms for optimized sample of -1W/g or less.
- Peak heights for initial coated sample exotherms are less than -2W/g.



C/20 Steady State Cycling Voltage Profile: Cycle 2

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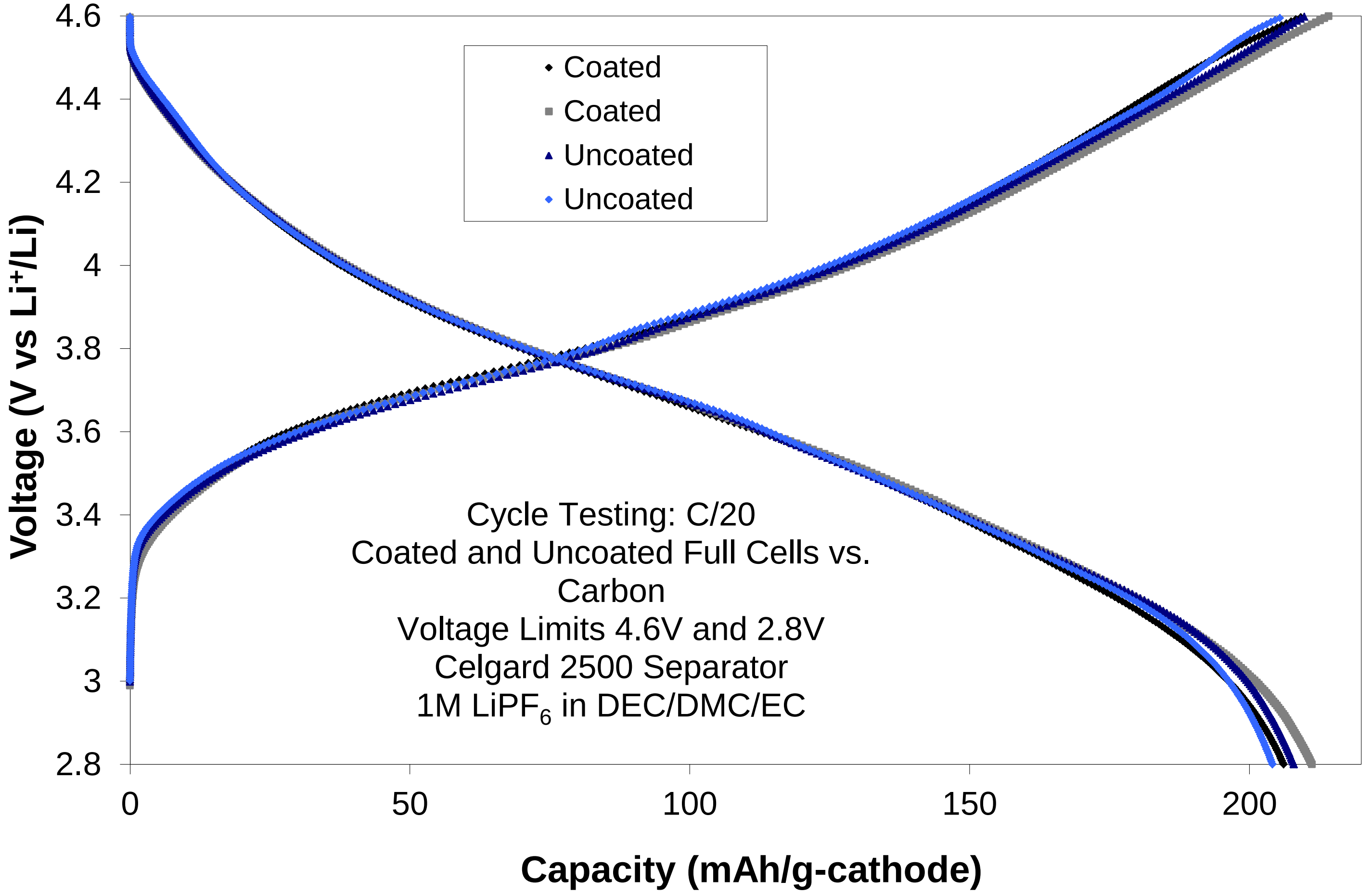
- **Discharge capacity of coated cells is 211 and 206mAh**
- **Discharge capacity of uncoated cells is 208 and 204mAh**
- **No observed difference in voltage trace**



Variable C-rate Cycling of Coated TODA

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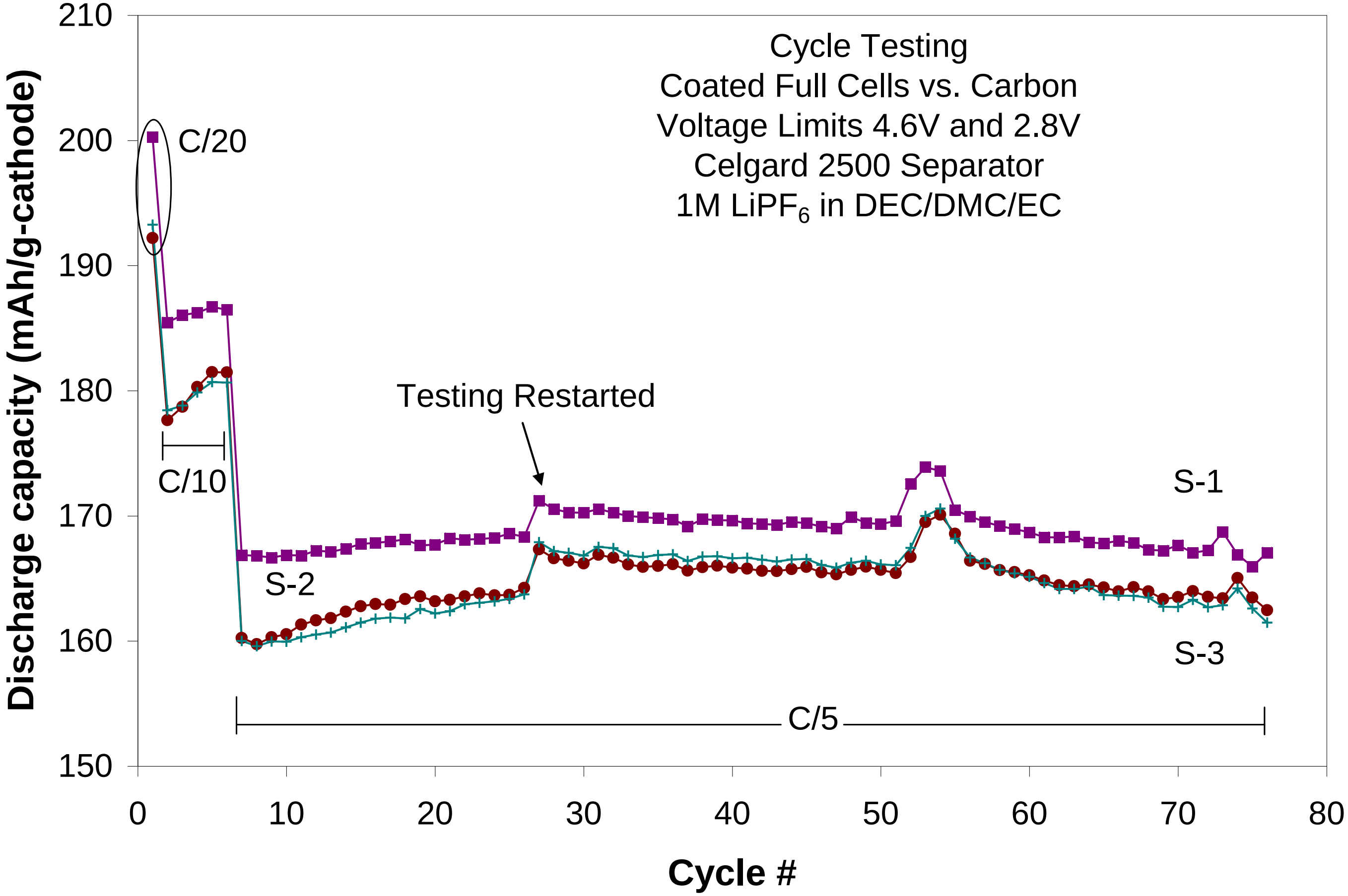
- Variation in capacities results from slight variation in anode to cathode ratios
- Cells cycled on initial 26 cycle procedure and then for an additional 50 cycles at C/5
- For each cell, capacity on cycle 76 is equal or higher than capacity on cycle 6



First Cycles for Coated and Uncoated Pouch Cells

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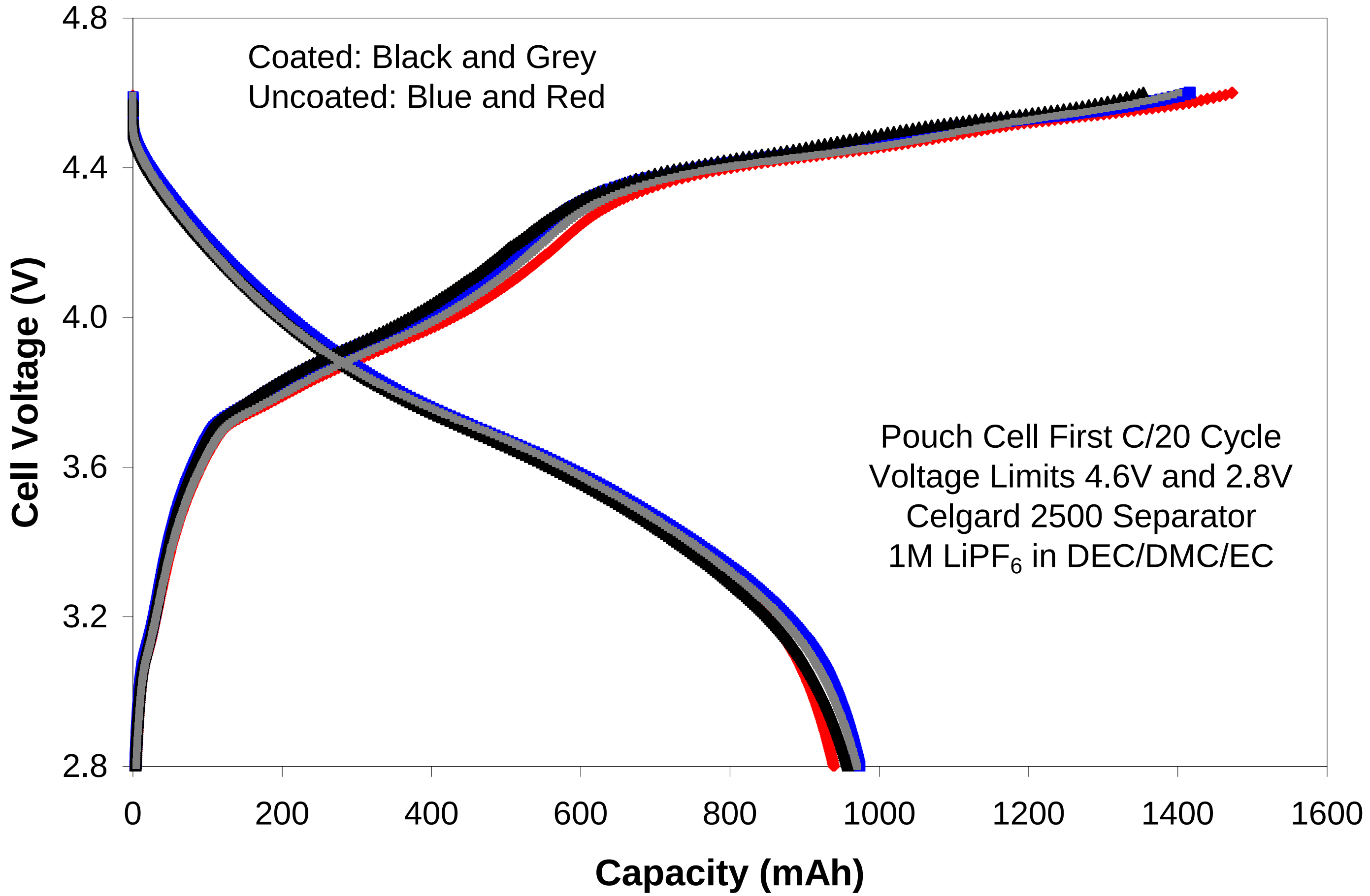
- Pouch cells were conditioned at C/20 between 4.6 and 2.8V
- First cycle efficiency is ~69% for each cell
- Initial discharge capacity is consistent with coin cell experiments



Third Cycle for Coated and Uncoated Pouch Cells

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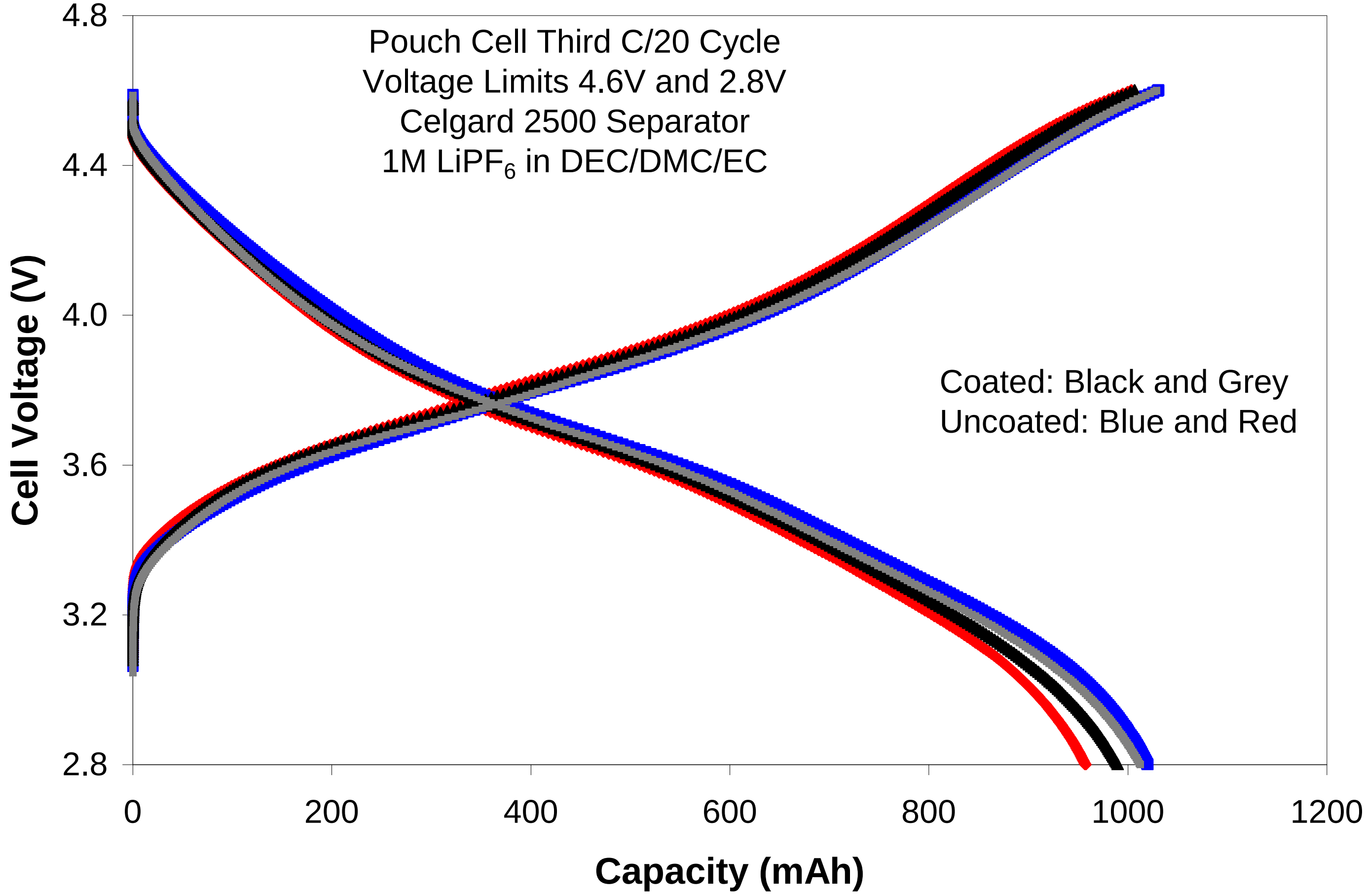
- Final C/20 cycles before overcharge.
- No polarization observed for coated or uncoated cells.
- Cell capacity is similar for coated and uncoated pouches.



Uncoated Cell Discharge Capacity after Abuse Testing

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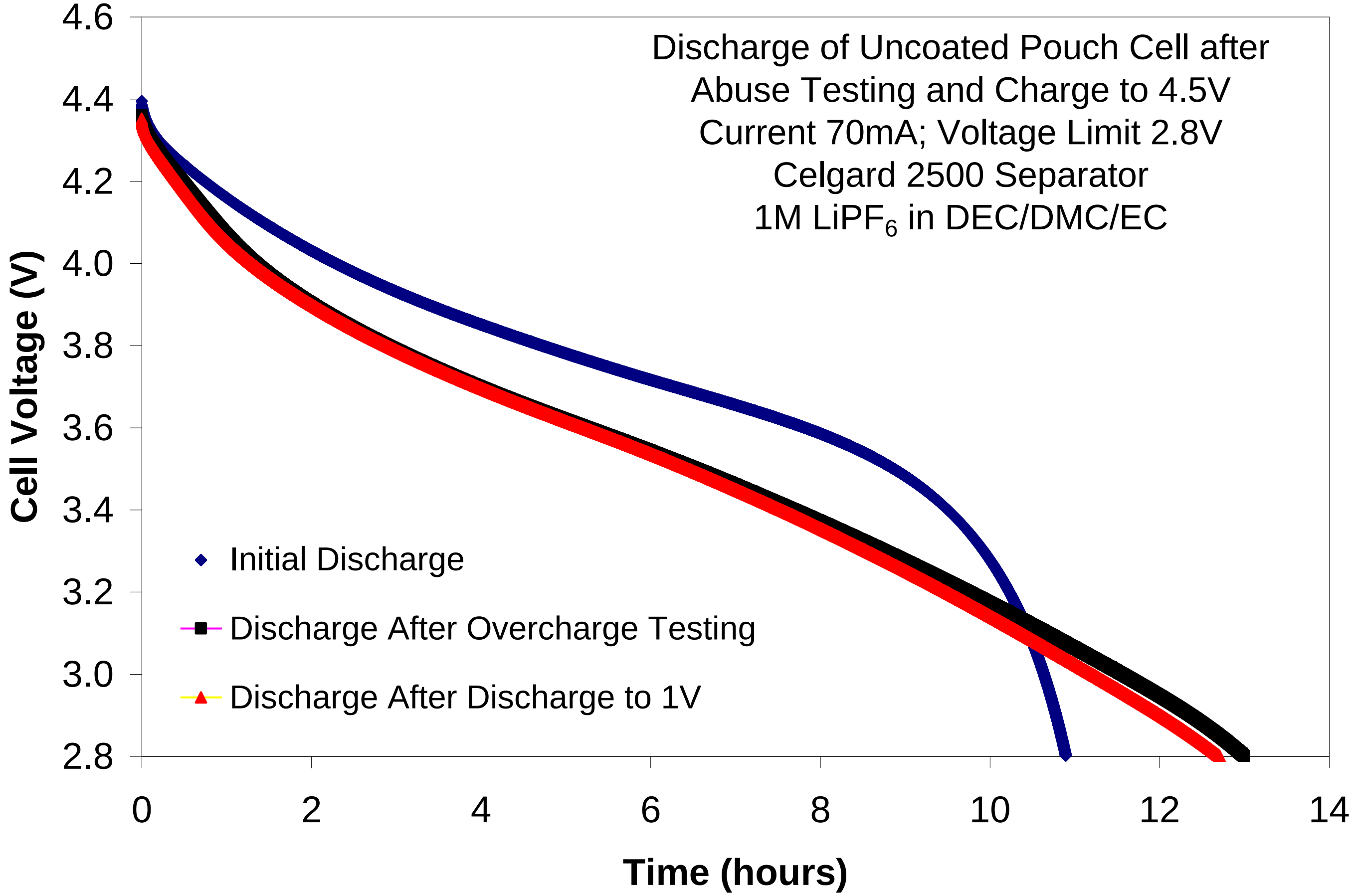
- All tests performed by charging to 4.5V at C/10.
- After overcharge testing to 5.5V, the cell capacity was 0.9Ah vs. 1Ah after 4.8V charge.
- After short-circuit test, the cell capacity was 0.88Ah.
- No observable cell damage noted due to testing.



Coated Cell Discharge Capacity after Abuse Testing

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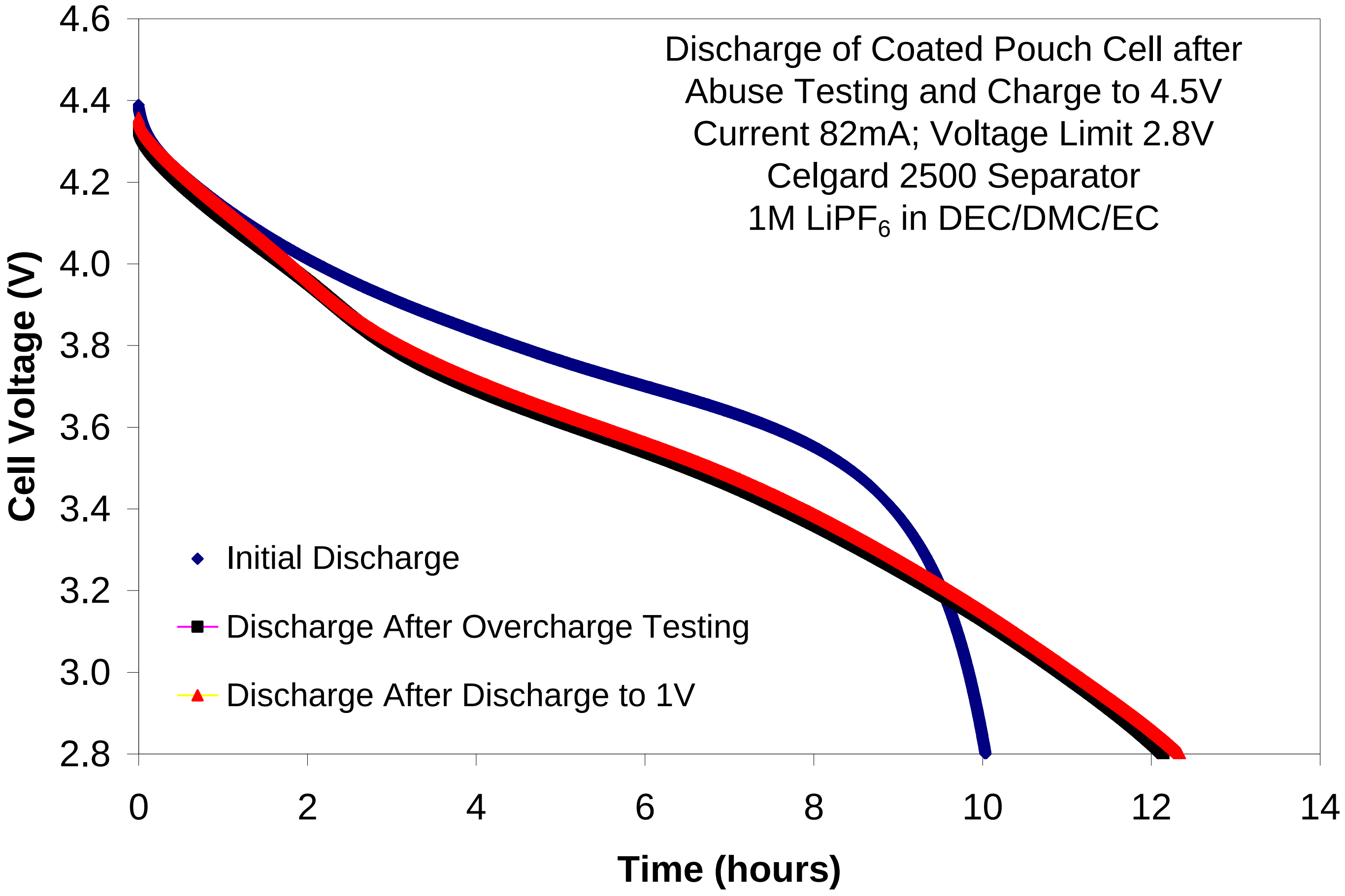
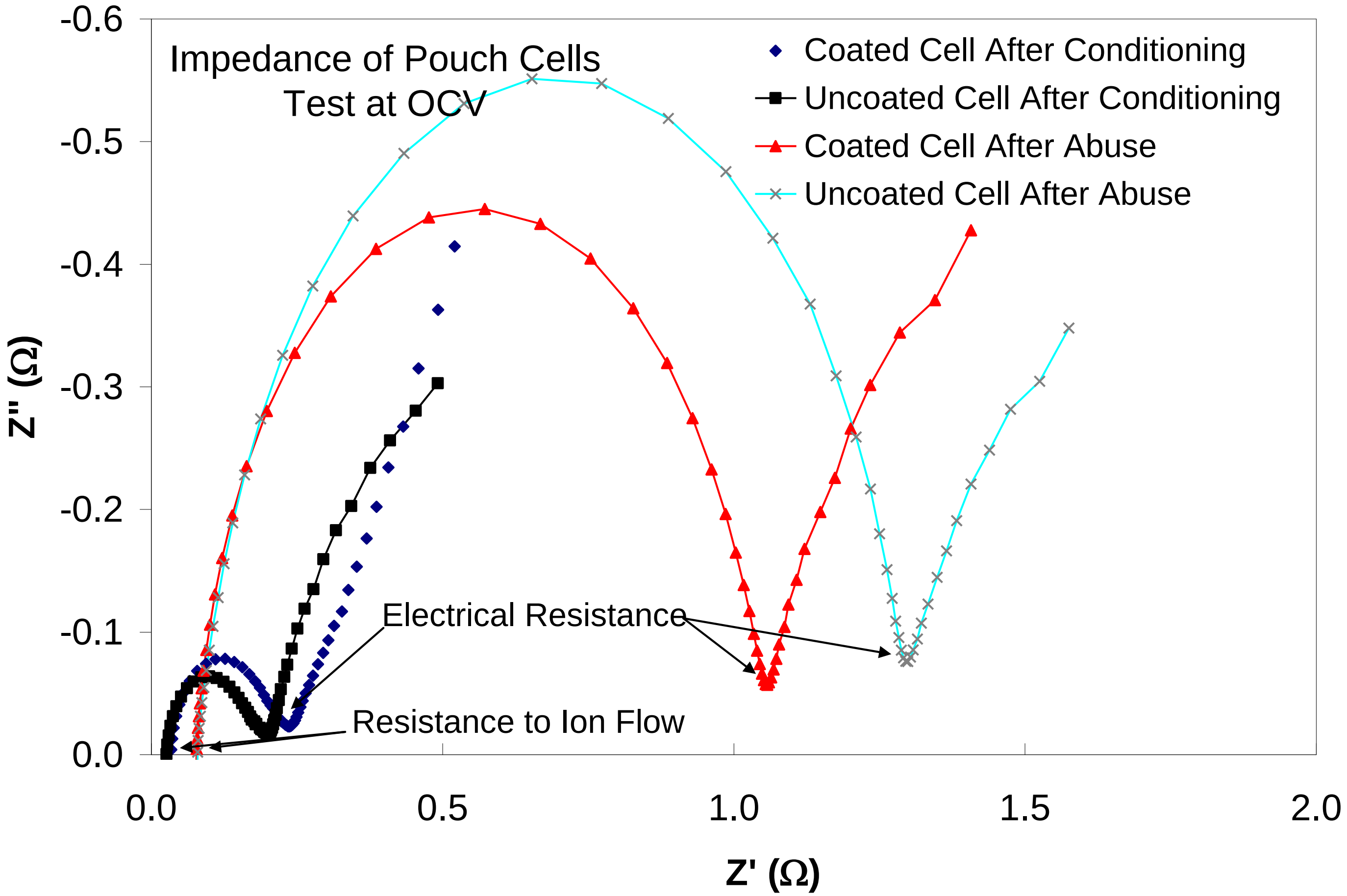
- All tests performed by charging to 4.5V at C/10.
- After overcharge testing to 5.5V, the cell capacity was 1Ah vs. 1.05Ah after 4.8V charge.
- After short-circuit test, the cell capacity was 1.01Ah.
- No observable cell damage noted due to testing.



Impedance Testing Before and After Abuse Testing

- Initially the ionic conductivity of the two cells is nearly equivalent with slightly higher electrical resistance for the coated cell.
- After overcharge and short-circuit testing ionic conductivities remain similar though electrical resistance for the uncoated cell increases more than for the coated cell.



Impedance Testing after Storage at 90°C

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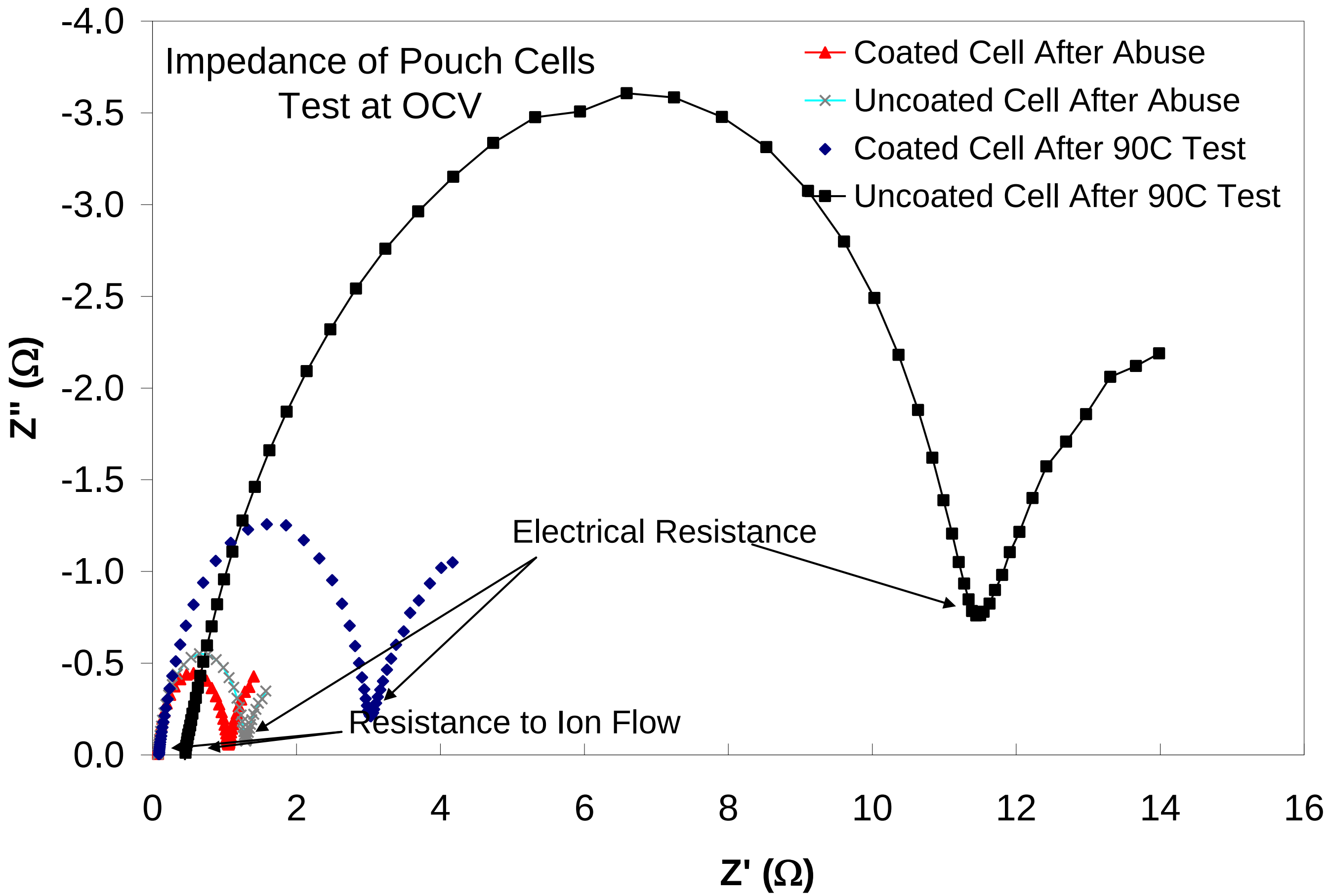
- Uncharged pouches placed in oven at 90°C for 5.5 hours.
- Neither cell catastrophically failed, but the uncoated cell appeared to lose some vacuum.
- Coated cell demonstrated increase in electrical resistance, but not ionic resistance.
- Both the electrical and ionic resistance for the uncoated cell increased by >3X.



Summary of Cathode Coating Results

- Optimized coating procedures for coating TODA cathode material.
- Coating reduces exotherms observed on heating delithiated cathode material from greater than -5W/g to less than -1W/g.
- Coated cathodes demonstrated <1% loss in discharge capacity over 50 cycles at a C/5 rate.
- Demonstrated scale-up with construction of 1Ah pouch cells:
  - No reduction in discharge capacity or voltage observed.
  - On abuse testing pouch cells utilizing coated cathode material demonstrated improved stability with reduced impedance growth on abuse testing.
- Successfully scaled-up cathode coating to produce and deliver 1500grams of coated cathode material.

Outline

- Metal Phosphate Coating for Improved Cathode Material Safety
- **Electrochemical Performance of Silicon Whisker and Carbon Nanofiber Composite Anode**
  - Background, overview and previous results
  - Scale-up efforts
  - Full cell performance
- Summary and Next Steps

Current Silicon Anodes

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Silicon anodes reported in the literature*:

1. Pure Si micro- and nano-scale powder anodes,
2. Si dispersed in an inactive matrix,
3. Si dispersed in an active matrix,
4. Si anodes with different binders,
5. Si thin films.

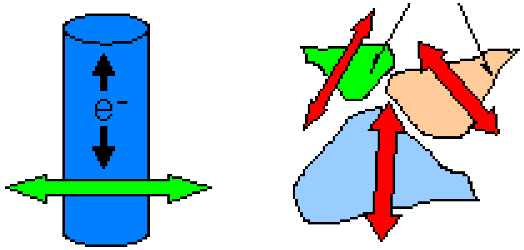
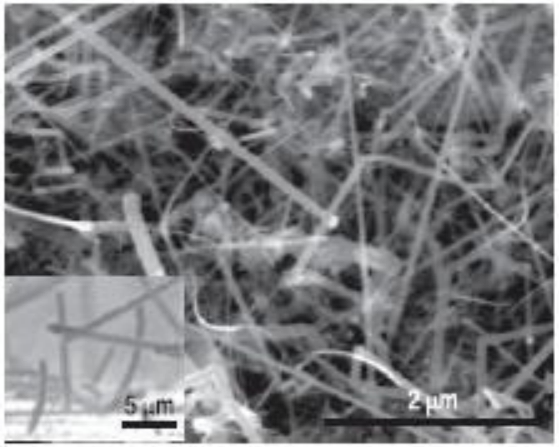
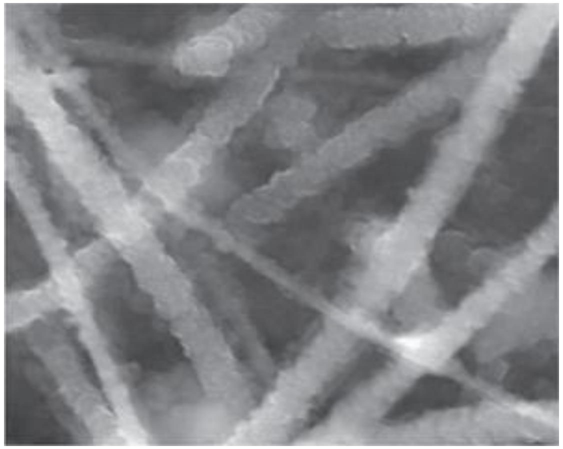


Illustration of destructive stress incurred by volume change during electrochemical cycling.

Silicon nanowire based anode by Chan et al. **:





Silicon nanowire on Stainless steel

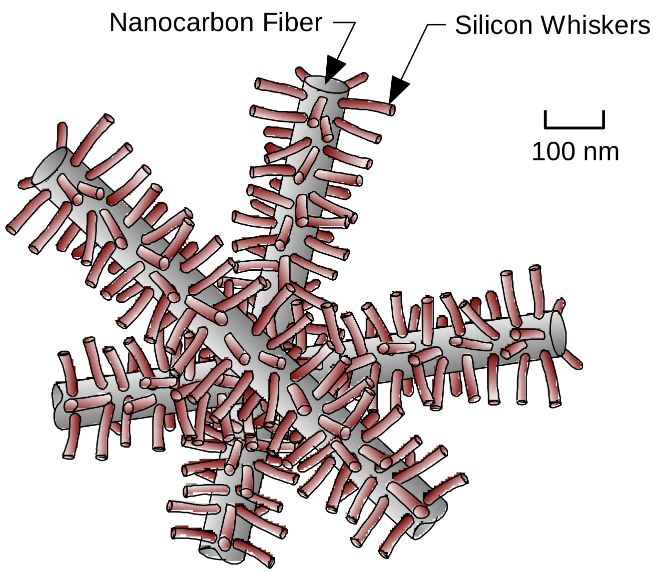
After cycling

- Demonstrated high capacity and rate capability

* U. Kasavajjula, C. Wang and A. J. Appleby, *Journal of Power Sources*, 163, 1003–1039, (2007).

** C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R. A. Huggins and Y. Cui, *Nature Nanotechnology*, 3, 31 – 35. (2008).

PSI Concept: Formation of a Silicon Whisker and Carbon Nanofiber Composite



Silicon Whiskers/Nanowires on Carbon Nanofiber

J-8382

Material Advantages:

- High in free volume;
- Free of polycrystalline domains (not achievable for silicon anode by CVD);
- Tailorable silicon loadings;
- Supporting matrix forms an electronically conductive framework;
- Processable using established procedure and equipment.

Cycle Life Performance of the Silicon Whisker/Carbon Fiber Composite

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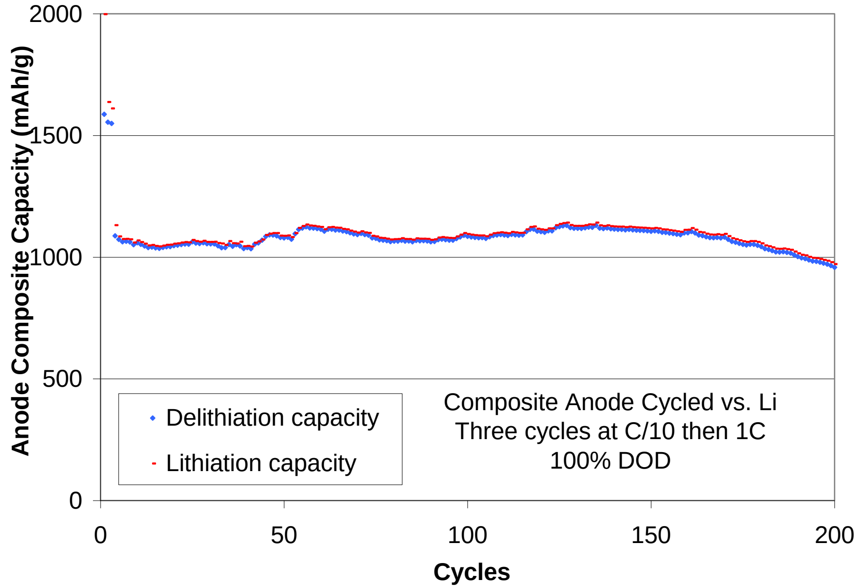
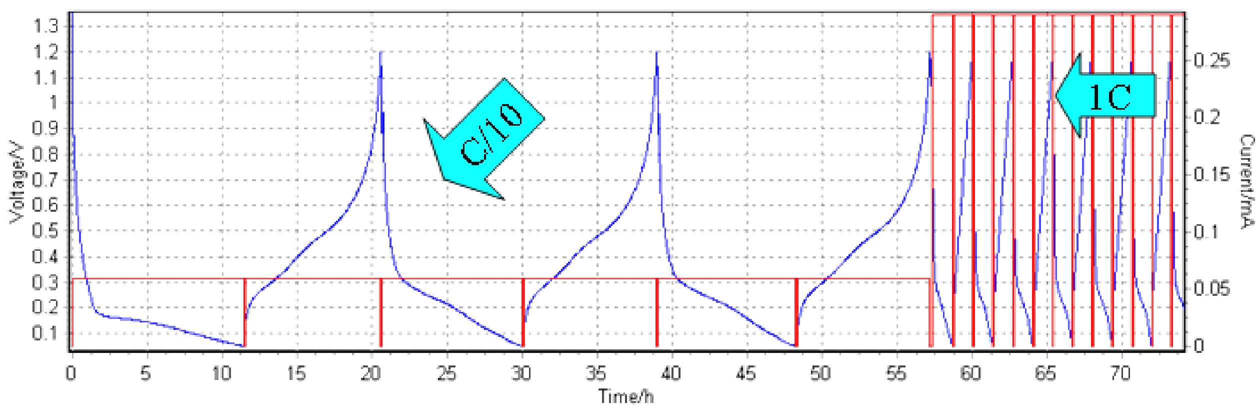


Discharge: anode lithiation; Charge: anode de-lithiation
All capacity values were calculated based on composite weight



- **Silicon-on-fiber architecture demonstrated with growth proportional to reaction time.**
- **Good cycle life achieved for > 200 cycles;**
- **C/10 cycles seems to be necessary to stabilize the cell;**
- **Single crystalline silicon whiskers are capable of cycling at high rate of 1C**

Successful Material Production Scale-up

- **Following initial property demonstration, research efforts focused on moving from producing ~0.5g to 50grams of material per batch.**
  - Progressively larger batches were run demonstrating linearity and scalability of the composite formation process.
  - Agitation of the sample provides for uniform deposition\material formation.
  - PSI has larger reactors that will be utilized for further material production scale-up efforts.
- **Electrode optimization has focused on improving the electrode uniformity to allow for continuous anode material production.**
  - PSI is producing sufficient electrode for Ah-sized cells and in follow-on efforts will work to demonstrate electrode production at a pilot casting facility.

Rate Performance of Initial High Loading Electrodes

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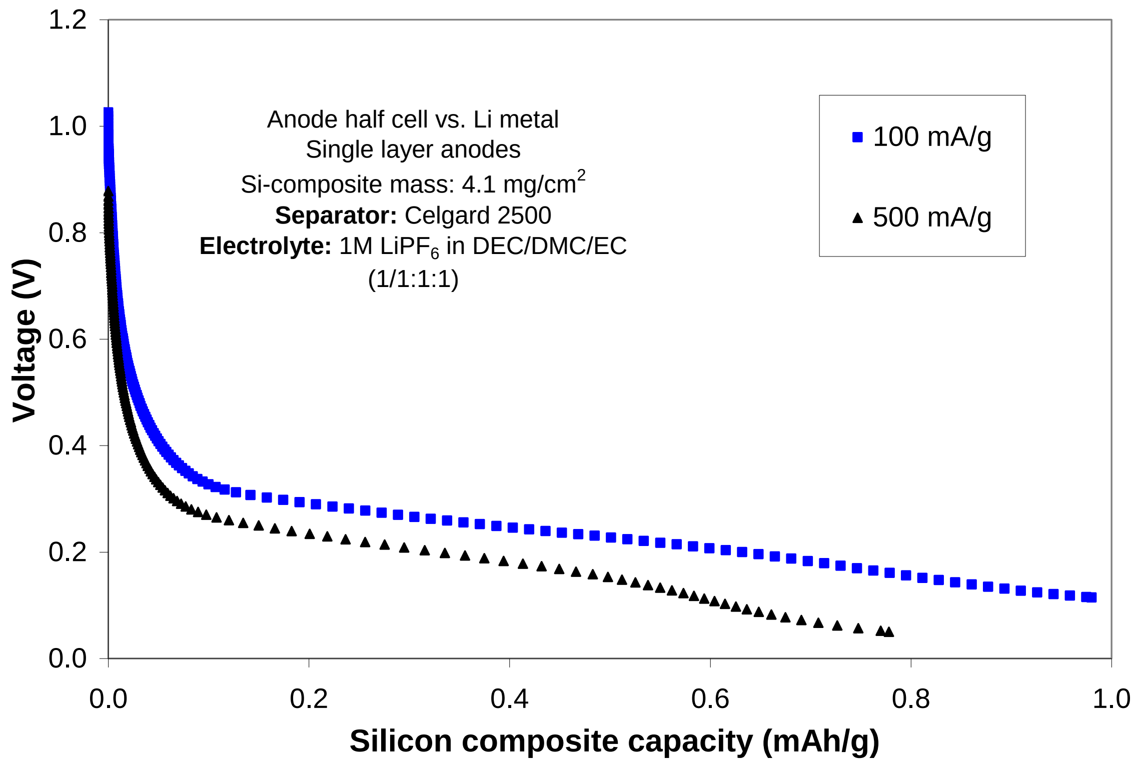
- **Research has been focused on increasing the material loading from ~0.5mAh/cm² to ~3-4mAh/cm².**
- **At low rates, capacities >1000mAh/g-composite were still achievable.**
- **Upon increased rate testing significant polarization was observed resulting in reduced performance.**



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Improved Performance on Process Optimization

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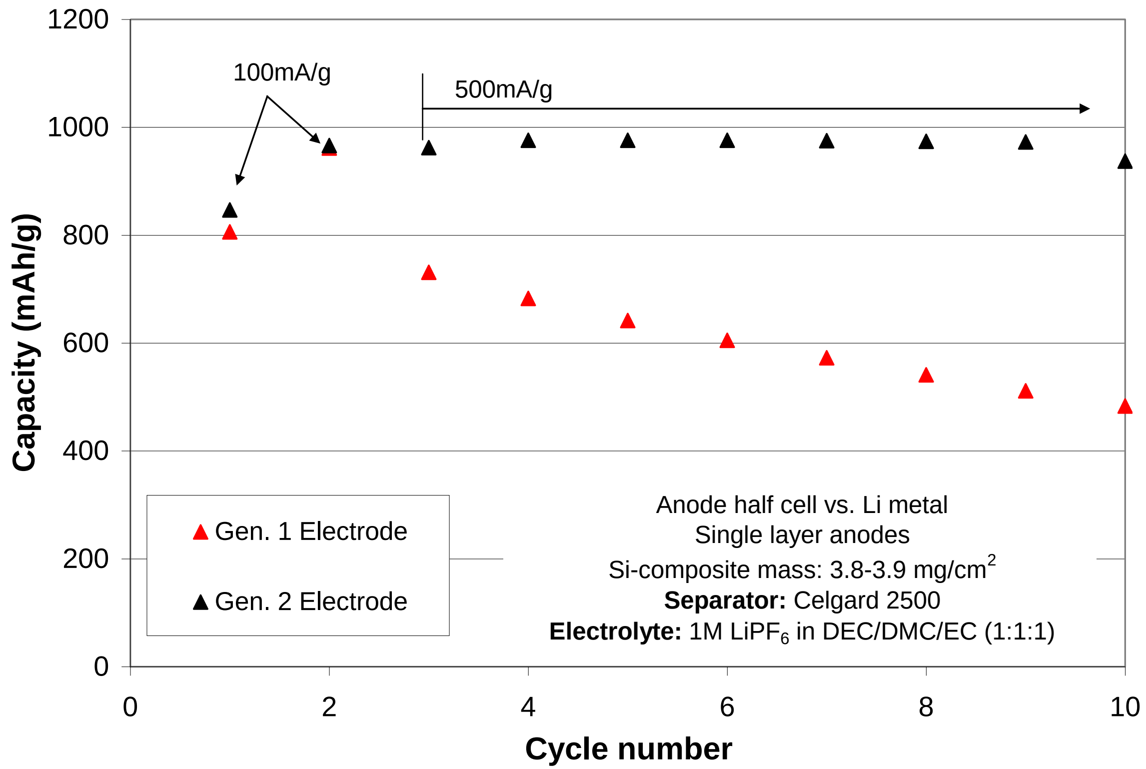
- **Testing of electrodes in half-cells at C/10 and C/2 was performed to determine the impact of different processing procedures on performance.**
- **Processing of the composite and slurry was adjusted to improve the cast uniformity and performance resulting in reduced performance fade on half-cell cycling at C/2 rates.**



Successful Transition from Coin to Pouch Cell

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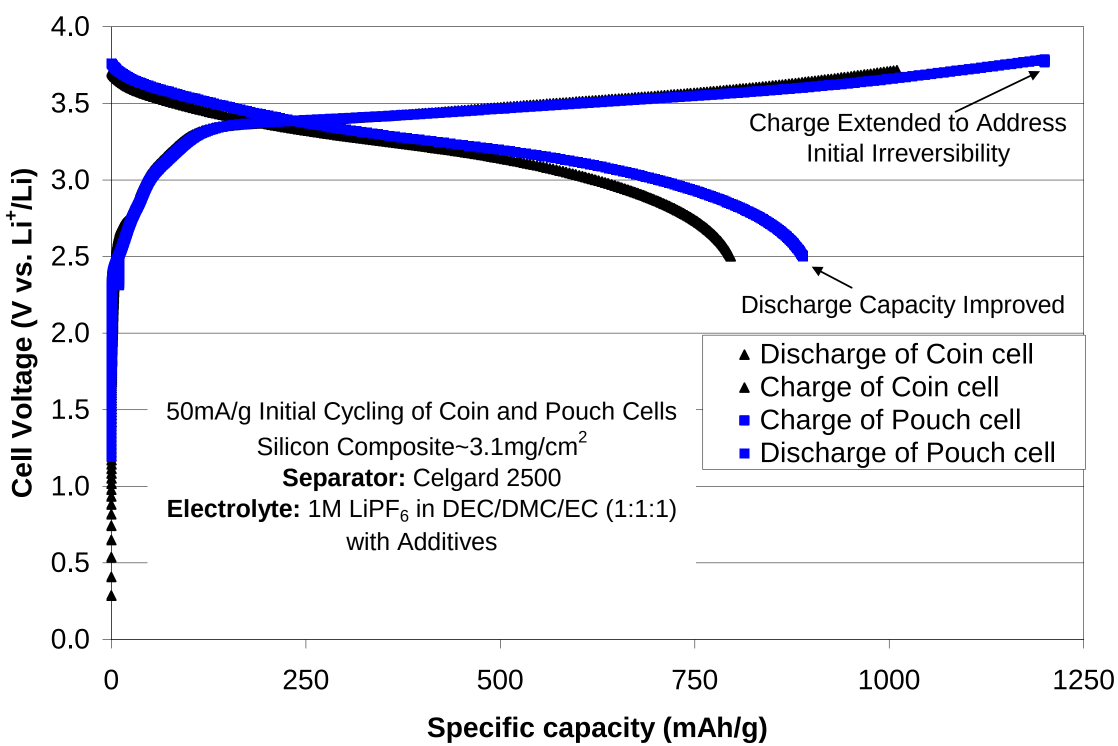
- **Pouch cells of ~75 and ~150mAh have been constructed to demonstrate the bulk properties of the electrodes and materials.**
- **Initial cycle at 50mA/g-composite was performed to compare coin and pouch cell performance.**
- **First cycle reversibility is 80-85% using this type of initial cycling procedure.**



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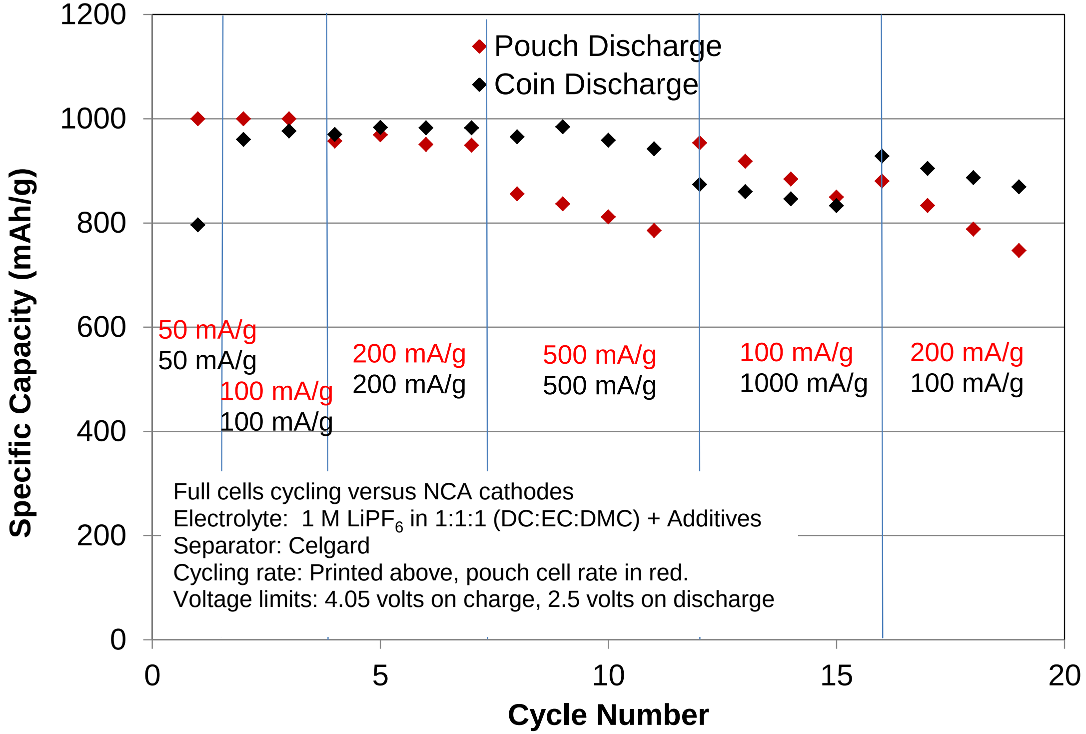
Full Cell Performance Demonstration

- **Coin and pouch cells were tested at various rates with similar performance measured for each type of cell.**
- **Utilizing the silicon anode 2.5Ah pouch cells have been designed and are being built. These cells will offer a 7% increase in the cell energy density as compared to using graphite anode material. The silicon anode reduces the anode material weight from 15-20% of the total cell mass to 6-8% of the total cell mass.**



Silicon Anode Program Summary

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- PSI has developed a silicon whisker and carbon nanofiber composite material capable of reversibly delivering >1000mAh/g at up to 1C rates.

- Composite fiber production has been successfully scaled to 50 gram scale, with a clear path to production of 250-500 gram batches.

- Electrode formulation optimized to produce electrodes delivering 1000mAh/g at the desired loadings.

- Equivalent pouch (150+mAh) and coin cell performance demonstrated.
  - Production of 2.5Ah pouch cells to be completed as part of research effort.

Outline

- Metal Phosphate Coating for Improved Cathode Material Safety
- Electrochemical Performance of Silicon Whisker and Carbon Nanofiber Composite Anode
- **Summary and Next Steps**

Summary of NASA Sponsored Battery Material Development Efforts

- PSI has successfully developed a cathode coating process that improves the cycling and safety performance of high energy density cathode materials.
- PSI has developed a silicon whisker and carbon nanofiber composite material capable of reversibly delivering >1000mAh/g at up to 1C rates.
- PSI has successfully demonstrated scale-up of the anode and cathode technologies and has developed a clear path to further scale-up.
- Equivalent performance in the coin and pouch cell formats demonstrates PSI ability to successfully scale-up and transition these novel technologies to a sufficient scale for application based testing.
- Future funded research effort will construct cylindrical cells utilizing composite silicon anode and high energy density cathode materials.

Acknowledgements

- **Anode Program:**
  - Special thanks to NASA for supporting this program under contracts NNX09CD30P and NNX10CA51C.
  - Dr. Richard Baldwin, William Bennett and the NASA Glenn Battery Group

    Electrochemistry Branch

    NASA Glenn Research Center, Cleveland, Ohio

- **Cathode Program:**
  - The cathode work was supported by NASA Johnson Space Center, Houston, TX 77058 and NASA Glenn Research Center, Cleveland, OH 44135 under a NASA NRA (contract # NNC09CA04C).
  - Special thanks to:
  - Dr. Judith Jeevarajan (COTR), Thomas B. Miller, Jon S. Read, and Pranav Patel for their assistance during the program.

- **All past and present PSI staff who have helped in the execution of these programs including:**
  - **Kara Constantine, Junqing Ma**, Ngoc Do, Alex Elliott, Michael McAllister, Peter Moran, Aron Newman, Nihala Thanikkal, Jose Vega

Thank you for your time.
Any Questions?

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